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Emulsifier effects on fat crystallisation

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ABSTRACT

The effect of the addition of two emulsifiers differing in their molecular structure (mono and di glycerides and Tween 80) on the thermal behaviour of a bulk fat containing both solid and liquid components (75% coconut oil and 25% of sunflower oil) was investigated using differential scanning calorimetry (DSC). Different ratios of emulsifier to bulk fat were considered (emulsifier/bulk fat of 0.02, 0.05, 0.08, 0.1, 0.3, 0.6 and 1). Both the emulsifiers had an effect on the melting and crystallisation of the bulk lipid. Mono and di glycerides (MDGs), although crystallising independently of the bulk fat (i.e. the observation of the presence of independent melting peaks and enthalpies that were not dependent on the ratio of MDGs to bulk fat), were thought to act as templates for the crystallisation of the bulk fat, having an effect on the shape of the melting and crystallisation peaks. Tween 80, due to its structural properties (unsaturated carbon chain and large hydrophilic head) was thought to act as an impurity leading to the formation of less perfect crystals and a loosely packed lattice, resulting in less energy required to melt. Due to the bulk fat and emulsifiers used this work has relevance to the ice cream industry, and could have implications for the physical properties of ice cream, particularly partial coalescence during manufacture, meltdown properties, texture and sensory perception during consumption.

1. Introduction

The effect of emulsifiers on fat crystallisation has been well documented (Wright, Hartel, Narine, & Marangoni, 2000; Wright & Marangoni, 2002; Litwinenko, Singh, & Marangoni, 2004; Fredrick, Foubert, Van De Sype, & Dewettinck, 2008; Basso et al., 2010). Depending on the homogeneity between the emulsifier and the lipid in terms of chain length and degree of saturation, emulsifiers can retard or accelerate nucleation, crystal growth, and/or polymorphic transitions (Garti, 1988; Garti & Yano, 2001). In the ice cream industry, two emulsifiers are commonly used: Tween 80 (polysorbate 80) and mono and di glycerides (MDGs) (Hartel & Goff, 2013). These two emulsifiers are different in their structure: Tween 80 is more hydrophilic (due to the polyoxyethylated sorbitol hydrophilic head) and has a bent carbon chain; MDGs have straight carbon chains and glycerol hydrophilic heads, making them more hydrophobic than Tween 80 (Euston, 2008).

It has been reported that polysorbates with saturated chains (such as Tween 40 or Tween 60) can act as seeds and promote fat crystallisation (reducing the free energy required for nucleation) and co-crystallise with the fat enhancing fat crystal growth. This effect is probably due to the similarity between the saturated carbon chains of the fat and the emulsifiers. In fact, Litwinenko et al. (2004) reported higher rate of crystal growth, smaller crystallites, and shorter nucleation induction time in samples containing Tween 60

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in comparison with samples without emulsifier. Sorbitan esters are similar emulsifiers to polysorbates, but with lower hydrophilicity because of the lack of the polyoxyethylene groups attached to the sorbitol molecule (Euston, 2008). The effect that these emulsifiers have on the crystallisation has been studied for a fat blend containing palm oil (Garbolino, Bartoccini, & Flöter, 2005), showing that long chain emulsifiers with at least 16 carbon atoms (sorbitan monopalmitate and sorbitan monostearate) will allow for optimal chain–chain interactions and result in co-crystallisation of the emulsifier and the fat, whose major fatty acids are palmitic and oleic acid, whereas sorbitan monolaurate has a shorter carbon chain which prevents interaction between the fat and the emulsifier.

Fredrick et al. (2008) showed that unsaturated monoacylglycerols (MAGs) from sunflower oil did not have an effect on the nucleation of palm oil crystals, whereas saturated MAGs (derived from palm oil) promoted nucleation. These authors suggested that the homogeneity between the fatty acids of MAGs and palm oil and their degree of saturation were the principal causes of the acceleration of palm oil crystallisation. MAGs can associate as reverse micelles (Walstra & Van Beresteyn, 1975), which can decrease the energy barrier for the nucleation of triacylglycerols (TAGs). If the MAGs are from palm oil they can form micelles and crystallise because of their higher melting point compared to MAGs from sunflower oil. Subsequently, these MAGs micellar crystals may act as seeding material and are more effective than micellar structures alone at promoting earlier nucleation. Foubert, Vanhoutte, and Dewettinck (2004) showed that the degree on saturation is an important factor in terms of the effect of the emulsifier on the fat. These authors investigated the influence of diacylglycerols (DAGs) and MAGs on the crystallisation of milk fat, showing that it was dependent on the acyl groups present in the additives. With stearic acyl chain the crystal growth rate was reduced, whereas an oleic acyl chain had no effect. The reason probably resides in the fact that stearic based MAGs and DAGs may be easily incorporated into the crystal lattice impeding further growth, whilst oleic based MAGs and DAGs are incorporated to a lesser extent due to their unsaturated carbon chain. The importance of the similarity between the fat and the emulsifier structure has also been highlighted by Smith, Cebula, and Povey (1994) and Smith and Povey (1997) who discussed the effect of different additives on the crystallisation of a trilaurin model system. The crystal growth rate increased in the presence of monolaurin, while it was hardly affected by MAGs, whose chain length differs from lauric acid. This was probably due to the co-crystallisation of monolaurin with trilaurin, which was not possible for emulsifiers with a different carbon chain length due to structural diversity. More recently, Basso et al. (2010) showed that the addition of MAGs accelerated the crystallisation of palm oil by increasing the number of crystallisation seeds (heteronuclei).

To conclude, there is a well-documented effect of the emulsifiers on fat crystallisation. In particular, depending upon the affinity between the emulsifier and the fat (saturation and carbon chain length) emulsifiers can interact with the fat favouring or interfering with the fat crystallisation.

The aim of this study was to investigate the thermal behaviour of a fat blend of 75% coconut oil and 25% sunflower oil in presence of Tween 80 and MDGs. The intention for the work was to investigate both a bulk fat blend and emulsifiers that have relevance for the production of ice cream; as such this was considered a model system to understand the effect in an emulsified ice cream. This is a novel area of investigation for two reasons: (1) the thermal behaviour of this blend has not been investigated previously and the effect of the presence of liquid oil on the crystallisation of coconut oil is required as it can decrease its crystallisation and increase its melting temperature (Norton, Spyropoulos, & Cox, 2009); (2) the effect of these two emulsifiers on the thermal behaviour of this fat blend has also not been investigated previously, and the effect of chain length and hydrophobicity of the head is interesting and useful for the scientific community as it is likely to have an impact upon the microstructure of ice cream. Our hypothesis is that Tween 80 interferes with the fat crystallisation (due to the unsaturated carbon chain and large hydrophilic head), whereas MDGs co-crystallise with the fat (due to the structural homogeneity with the bulk fat), favouring its crystallisation.

The results are likely to have many applications in the ice cream industry. This fat blend is an economic substitute to milk fat as it mimics milk fat it in terms of partial coalescence, meltdown behaviour and flavour.

2. Materials and methods

2.1. Materials

Sunflower oil was purchased from a retailer (Sainsbury's, UK); coconut oil was purchased at Akoma International (UK) Ltd. MDGs (product number: 149563) were purchased at Danisco (UK) Ltd and Tween 80 (product number: 9005-65-6) was purchased at Croda (EU) Ltd. MDGs were palm based (saturated 16-carbon chain) and mono glycerides represent more than 60%. Most abundant fatty acid in coconut oil and sunflower oil were lauric acid (saturated 12-carbon chain) and linoleic acid (unsaturated 18-carbon chain) respectively.

2.2. Preparation of the fat-emulsifier blends

The fat blend used was a blend of coconut oil 75% and sunflower oil 25% (bulk fat). Emulsifiers, Tween 80 and MDGs were dispersed at different ratios (emulsifier/bulk fat of 0.02, 0.05, 0.08, 0.1, 0.3, 0.6 and 1) in the melted bulk fat and stirred with a magnetic stirrer at 80 °C for approximately 20 min, until a homogeneous sample was obtained.

2.3. Differential scanning calorimetry

The effect of the emulsifiers on the thermal behaviour of the bulk fat used was determined using differential scanning calorimetry (DSC), a Perkin Elmer DSC Series 7 (UK), with thermal analysis software (Pyris). Nitrogen was used as a purge gas, at a flow rate of 30 ml/min. The thermal behaviour of MDGs was also measured. The samples (8–10 μg) were loaded into Perkin Elmer 40 μl capacity aluminium pans, and sealed with aluminium covers; an empty pan was used as a reference. The following thermal programme was used: holding isothermally at 70 °C for 10 min, cooling from 70 °C